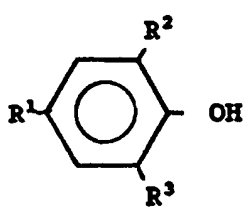




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C08G 65/48, C07C 43/23, 41/14</b>	<b>A1</b>	(11) International Publication Number: <b>WO 96/01865</b> (43) International Publication Date: 25 January 1996 (25.01.96)
(21) International Application Number: <b>PCT/NL95/00242</b> (22) International Filing Date: 10 July 1995 (10.07.95) (30) Priority Data: 9400644                      11 July 1994 (11.07.94) <b>BE</b> (71) Applicant (for all designated States except US): <b>DSM N.V.</b> [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): <b>OEVERING, Henk</b> [NL/NL]; Burg. Eussenstraat 46, NL-6181 BR Stein (NL). <b>WERUMEUS BUNING, Gerard, Hidde</b> [NL/NL]; Past. Meulenbergstraat 20, NL-6438 HZ Schinnen (NL). <b>MEIJER, Egbert, Willem</b> [NL/NL]; Schoenmakerslaan 7, NL-5583 GC Waalre (NL). <b>VAN AERT, Hubertus,</b> <b>Adrianus, Maria</b> [NL/NL]; Overbergseweg 9, NL-4635 <b>RG Huybergen</b> (NL). <b>OUT, Gerardus, Jacobus, Joseph</b> [NL/NL]; Wolkammersdreef 59c, NL-6216 RM Maastricht (NL). (74) Agent: <b>SCHELTUS, Irma</b> ; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: <b>AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).</b>  Published <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>
(54) Title: <b>MULTIHYDROXY-FUNCTIONAL OLIGOPHENYLENE OXIDE</b>  <div style="text-align: center;">  <p>(I)</p> </div> (57) Abstract  Multihydroxy-functional oligophenylene oxide obtainable by reacting a compound containing hydroxyaryl comprising at least three hydroxyaryl groups according to formula (I), wherein R <sup>1</sup> = an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms, R <sup>2</sup> , R <sup>3</sup> = H or an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms, or two of the R <sup>1</sup> , R <sup>2</sup> or R <sup>3</sup> groups together constitute a ring structure containing 4-50 carbon atoms with a polyphenylene oxide in the presence of a catalyst complex comprising a transition metal and and amine.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

MULTIHYDROXY-FUNCTIONAL OLIGOPHENYLENE OXIDE

5

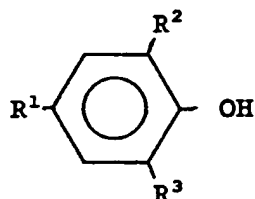
The invention relates to multihydroxy-functional oligophenylene oxide.

Mono- and dihydroxy-functional oligophenylene oxides are known from GB-A-1,119,914. This publication describes mono- and difunctional oligophenylene oxides that are prepared by a reaction between poly-(1,4-phenylene oxide) and a mono- or diphenol. This reaction is activated by the presence of an initiator, such as a peroxide or a catalyst containing a copper compound.

The aim of the invention is the preparation of multihydroxy-functional oligophenylene oxides.

According to the invention these compounds are prepared by reacting a compound containing hydroxyaryl comprising at least three hydroxyaryl groups according to the formula

25



where

30  $R^1$  = an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,  
 $R^2, R^3$  = H or an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,  
or two of the  $R^1, R^2$  or  $R^3$  groups together constitute a  
35 ring structure containing 4-50 carbon atoms, with a polyphenylene oxide in the presence of a catalyst complex containing a transition metal and an amine,

This results in the preparation of multihydroxy-functional oligophenylene oxide in a practically pure form.

The multihydroxy-functional oligophenylene oxide  
5 has a high mechanical stability, in contrast with mono-  
and dihydroxy-functional oligophenylene oxides.  
The spherical multihydroxy-functional oligophenylene  
oxides obtained by reaction of, for instance a calixarene  
or a dendrimer with polyphenylene oxide are very suitable  
10 for use as a fluidity improving agent in other polymers,  
such as polyphenylene oxide and mixtures containing  
polyphenylene oxide.

According to the invention, the reaction between  
the compound containing hydroxyaryl and the polyphenylene  
15 oxide is carried out in the presence of a catalyst complex  
containing a transition metal and an amine.

As the amine, the catalyst complex may contain  
aliphatic amines or compounds containing pyridine, such as  
diethylamine, dibutylamine, tetramethylene diamine,  
20 oligomeric amines, polyvinyl pyridine, pyridine and  
dimethylaminopyridine.

Preferably the catalyst complex contains  
dimethylaminopyridine.

The catalyst complex also contains a transition  
25 metal. The transition metal is chosen from groups 8-11 of  
the Periodic System of the Elements (Handbook of Chemistry  
and Physics, 70th edition, CRC Press, 1989-1990).  
Preferably the transition metal is chosen from the group  
comprising copper, manganese, iron and cobalt.  
30 With particular preference the catalyst complex contains  
copper.

Examples of copper compounds which can be used  
are copper(I) chloride, copper(I) acetate or copper(I)  
carboxylate. The halides, acetates and carboxylates of  
35 copper(II) may also be used.

During the reaction of the polyphenylene oxide

with the compound containing hydroxyaryl a transesterification takes place, in which a hydroxyl-functional oligophenylene oxide is formed.

'Transesterification' is understood to mean: the  
5 redistribution of the phenol monomers constituting the polyphenylene oxide among the hydroxyaryl groups of the compound containing hydroxyaryl so that oligophenylene oxides with the same number-average molecular weight are formed. An oligophenylene oxide is formed as an 'arm' onto  
10 the compound containing hydroxyaryl.

'Oligophenylene oxide' is understood to mean an oligomer of phenol monomers containing at least one chain of monomers that comprises between 2 and 70 monomer units.

An advantage of the process for the preparation  
15 of the multihydroxy-functional oligophenylene oxides described above is that by this process the multihydroxy-functional oligophenylene oxides are obtained in a practically pure form in a simple way.

In principle, all compounds containing  
20 hydroxyaryl can be used as the compounds containing hydroxyaryl comprising at least three hydroxyaryl groups as defined by the above formula.

Examples of compounds containing hydroxyaryl comprising at least three hydroxyaryl groups are: star-shaped phenols,  
25 phenolic resins and other phenol-modified polymers, calix-(n)arenes and dendrimers containing terminal hydroxyaryl groups.

Examples of star-shaped phenols are: 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-tertiary-butylphenol,  
30 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-octylphenol, 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-isooctylphenol, 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-isopropylphenol, 2,4,6-tri-(4'-hydroxy-3',5'-dimethylbenzyl)phenol, (3,3',5,5'-tetra(4"-hydroxybenzyl)-  
35 4,4'-dihydroxyphenyl)methane, (3,3',5,5'-tetra(4"-hydroxy-3",5"-dimethylbenzyl)-4,4'-dihydroxydiphenyl)methane, 2,2-

- (3,3',5,5'-tetra(4"-hydroxy-3",5"-dimethylbenzyl)-4,4'-dihydroxydiphenyl)propane, 1,1-(3,3',5,5'-tetra(4"-hydroxy-3",5"-dimethylbenzyl)-4,4'-dihydroxydiphenyl)cyclohexane, 1,1,4,4-tetra(4-hydroxyphenyl)cyclohexane and 1,1,4,4-tetra(3,5-dimethyl-4-hydroxyphenyl)cyclohexane.

Resols and novolaks can be mentioned as phenolic resins.

Examples of other phenol-modified polymers are:

- 10 poly(p-hydroxystyrene), copolymers of p-hydroxystyrene and other monomers, terminal-hydroxyaryl-containing polycarbonate, polyetherimide and polysulphone. Calixarenes are metacyclophanes with a hydroxyl group at each 2 position. They are prepared via a base-catalysed  
15 condensation reaction of a p-alkylphenol and formaldehyde. They are for example described in 'Calixarenes, C.D. Gutsche, The Royal Society of Chemistry, Cambridge (1989)". Tertiary-butylcalix(4)arene, tertiary-butylcalix(6)arene  
20 and tertiary-butylcalix(8)arene can for example be mentioned as calixarenes.

- Dendrimers are three-dimensional, highly branched oligomeric and polymeric molecules with an exactly defined chemical structure. Dendrimers are  
25 generally composed of a core, a number of generations of branches and an external surface.

- The generations of branches are composed of structural units repeating themselves, which are radially bound to the core. The external surface is composed of the  
30 functional groups of the last generation. Examples of suitable dendrimers are for example described in Angew. Chem. Int. Ed. Engl. 29 (1990), pp. 138-175 and PCT/NL93/00008. As the functional groups in the external surface, the dendrimers that can be used according to the  
35 invention contain the hydroxyaryl groups according to the above formula. Examples of these dendrimers are: 4-

cascade: 1,4-diaminobutane[4]:N-T-BOC-L-tyrosine-propylamide, 8-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)<sup>4</sup>:N-T-BOC-L-tyrosine-propylamide), 16-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)<sup>12</sup>:N-T-BOC-L-tyrosine-propylamide), 32-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)<sup>28</sup>:N-T-BOC-L-tyrosine-propylamide) and 64-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)<sup>60</sup>:N-T-BOC-L-tyrosine-propylamide).

As polyphenylene oxide use can be made of all the known polyphenylene oxides, as for example described in 'Encyclopedia of polymer science and engineering, Vol. 13, John Wiley & Sons, Inc. (1988), pp 1-30'.

Hydroxyl-functional oligophenylene oxides can be used in a wide field of applications. The spherical multihydroxyl-functional oligophenylene oxides can for example be used as fluidity improving agents in other polymers. Also conceivable is a mixture of polyphenylene oxide and (a) multifunctional oligophenylene oxide(s) that makes the polyphenylene oxide better processable.

The multi-hydroxy-functional oligophenylene oxides can also be used as fluidity improving agents in mixtures of polyphenylene oxide with other polymers, such as polystyrene, polyamide-6,6 and polypropylene. Spherical multihydroxy-functional oligophenylene oxides are better mixable with other polymers than polyphenylene oxide. The oligophenylene oxides also possess a high chemical resistance.

To improve the mechanical properties of polymers they can be polymerised in thermosets, such as epoxy resin, (meth)acrylates, polyesters and silicones. Further multihydroxy-functional oligophenylene oxides improve the flame-retardant properties of thermosets.

The invention will be further illustrated with reference to the examples without being limited hereto.

### Examples

The materials and methods used:

- low-molecular-weight PPO: a PPO with an  $M_n$  of 3800,  $D = 2.5$ ;
- 5 -  $\text{Cu(I)Cl}$ , analytical reagent, from Merck;
- dimethylaminopyridine (DMAP): 99% DMAP from Janssen Chimica;
- the number-average molecular weight,  $M_n$ , was determined via  $^1\text{H-NMR}$  using a Bruker AM-400
- 10 spectrometer.

### Example I

5.003 g of PPO-OH ( $M_n = 8200$ ) and 0.6717 g of tertiary-butylcalix(8)arene were together dissolved in 250  
15 ml of chloroform. 0.0475 g of  $\text{CuCl}$  and 0.0974 g of DMAP were added as the catalyst. A 20:80 mixture of oxygen:nitrogen was bubbled through at 20 ml/min. The reaction was carried out for 40 hours at room temperature. The product was shaken out using a 10% EDTA solution. The  
20 product was precipitated from the chloroform phase using heptane.

The number-average molecular weight of the oligophenylene oxide formed was 11590. The average length of the oligophenylene oxide chains was  $n = 10.7$ .

25

### Example II

4.0 g of 2,6-bis(4'-hydroxy-3',5'-dimethylbenzyl)-4-isooctylphenol and 15.4 g of low-molecular-weight PPO were dissolved in 200 ml of  
30 chloroform. Then 0.12 g of  $\text{CuCl}$  and 0.24 g of DMAP in 50 ml of chloroform were added. After 5 hours' reaction under nitrogen, compressed air was passed over the mixture for 1.5 hours. After another 20 hours' reaction under nitrogen, compressed air was bubbled through for 2 hours.  
35 Then the reaction was continued for another 23 hours under nitrogen. Then the product was separated from the reaction



mixture, washed using a 10% HCl solution and dried. The number-average molecular weight of the oligophenylene oxide formed was 2764. The average length of the oligophenylene oxide chains was  $n = 5$ .

5

#### Example III

5.0 g of 2,6-bis(4'-hydroxy-3',5'-dimethylbenzyl)-4-isooctylphenol and 7.7 g of low-molecular-weight PPO were dissolved in 200 ml of chloroform. Then 0.11 g of CuCl and 0.25 g of DMAP in 50 ml of chloroform were added. After 24 hours' reaction under nitrogen, oxygen was passed over the solution for 15 minutes. Then 5.0 g of pyridine was added, after which the reaction was continued under nitrogen. After a total of 72 hours' reaction the product was separated from the reaction mixture, washed using a 10% HCl solution and dried. The number-average molecular weight of the oligophenylene oxide formed was 1102. The average length of the oligophenylene oxide chains was  $n = 2$ .

20

#### Example IV

##### Synthesis of a multihydroxy-functional oligophenylene oxide with $n = 4$

0.209 g PPO-OH ( $M_n = 2833$ ) and 0.0521 g poly(p-hydroxystyrene) ( $M_w = 30.000$ ) were dissolved in 10 ml tetrahydrofuran (THF), 2.5 mg CuCl and 5 mg DMAP were added as the catalyst.

After 3 days reaction under air heptane was added, causing the product obtained to precipitate.

30 In the same way as described above, but with other ratio's of PPO-OH versus poly-(p-hydroxystyrene) multihydroxy-functional oligophenylene oxides were prepared with  $n = 1$  and  $n = 20$ .

TABLE 1:

n	M <sub>n</sub>
1	3130
4	4200
20	8370

Example VSynthesis of a multihydroxy-functional oligophenylene oxide with n = 4

- 10                    5 g PP (Vestoran®, see table) and 1.41 g (2.3 mmol) 1,1,4,4-tetrakis(4-hydroxy-3,5-dimethylphenyl)cyclohexane (1) were dissolved in 60 ml boiling THF.
- 0.02 g CuCl and 0.042 g DMAP were added as the catalyst.
- 15 After the reaction mixture was refluxed for 24 hours 25 ml 10% HCl was added during stirring.
- The suspension formed was extracted 3 times with chloroform. The collected organic phases were washed with a saturated NaCl-solution, dried over Na<sub>2</sub>SO<sub>4</sub> and reduced by
- 20 evaporation. 5.58 g (87%) product was obtained.
- The amounts of (1), CuCl and DMAP were varied for the synthesis of the other polymers.
- The polymers obtained were characterised with <sup>1</sup>H-NMR and gelpermeation chromatography combined with a viscosity
- 25 detector.

TABLE 2:

oligomer n	$M_n$ (g/mol)	$M_w$ (g/mol) <sup>a)</sup>	$[\eta]$ (dl/g) <sup>b)</sup>
armlength 4	864	4800	0,130
armlength 8	2028	15500	0,245
armlength 16	3492	18700	0,285
armlength 32	5076	23000	0,319
armlength 64	7518	33800	0,387
Vestoran® -	9360	36800	0,472

- 10 a) the molecular weight was determined with  
gelpermeation chromatography according to ASTM-D  
3593-80
- b) the viscosity of each fraction was determined with a  
viscosity detector after gelpermeation chromatography  
15 was performed. This method is described in 'Journal  
of Liquid Chromatography' (1990); Yau W.W. & Rementer  
S.W.; Vol. 13, page 627.
- The Zimm-Stockmayer theory teaches that the value of  
the ratio between  $[\eta]_{\text{star}}/[\eta]_{\text{lin}}$  indicates the degree  
20 of branching.
- $[\eta]_{\text{star}}$  and  $[\eta]_{\text{lin}}$  must be determined on star-shaped  
and linear polymers with comparable molecular weight.  
Calculations of  $g' = [\eta]_{\text{star}}/[\eta]_{\text{lin}}$  show that the  
oligomers with armlength 8, 16, 32 and 64 have a  
25 degree of branching of 4.
- The calculations were performed in the way that is  
described in "Zimm, B.H. and Stockmayer, W.M.;  
Journal of Chemistry & Physics (1949), Vol. 17, p.  
1301", "Zimm, B.H. and Kilb R.W.; Journal of Polymer  
30 Science (1959), Vol. 37, p. 19" and Roovers J. et  
all; Macromolecules (1993), Vol. 26, p. 4324.

Examples VI-XIUsed Dendrimers:

- 4-cascade: 1,4-diaminobutane[4] : N-T-BOC-L-tyrosinepropylamide = DAB(PA)<sub>4</sub>-tyrosine
- 8-cascade: 1,4-diaminobutane[4] : (1-azabutylidene)<sup>4</sup> : N-T-BOC-L-tyrosinepropylamide) = DAB(PA)<sub>8</sub>-tyrosine
- 32-cascade: 1,4-diaminobutane[4] : (1-azabutylidene)<sup>28</sup> : N-T-BOC-L-tyrosinepropylamide) = DAB(PA)<sub>32</sub>-tyrosine
- 64-cascade: 1,4-diaminobutane[4] : (1-azabutylidene)<sup>60</sup> " N-T-BOC-L-tyrosine) and modifications hereof with less than 100% L-tyrosine-endgroups.

Example VI

- 0.150 g DAB(PA)<sub>8</sub>-tyrosine in 2 ml dimethylsulfoxide (DMSO) was slowly added to a solution of 1.14 g PPO (Mn= 5520) in 30 ml chloroform in an argon atmosphere.
- 11.5 mg CuCl and 25.4 mg DMAP were added as a catalyst.
- The solution was stirred for 4 weeks under argon. The product was obtained after shaking the solution with a 10% EDTA solution and a 10% HCl-solution, whereafter the solution was reduced by evaporation until 15 ml was left and was added to 200 ml methanol.

Examples VII-VIII

Example VI was repeated with DAB(PA)<sub>32</sub>-tyrosine and DAB(PA)<sub>64</sub>-tyrosine instead of DAB(PA)<sub>8</sub>-tyrosine.

Example IX

Example VI was repeated with 0.12 g DAB(PA)<sub>64</sub> (80% L-tyrosine; 20% d-phenylalanine) and 0.18 g PPO. 2.5 mg CuCl and 5.2 mg DMAP were added as the catalyst. Chloroform was used as a solvent for the dendrimer.

Example X

Example IX was repeated with 0.32 g DAB(PA)<sub>64</sub> (50% L-tyrosine; 50% d-phenylalanine) and 1.16 g PPO. 9.7 mg CuCl and 19.5 mg DMAP were added as the catalyst.

5

Example XI

Example IX was repeated with 0.12 g DAB(PA)<sub>64</sub> (20% L-tyrosine; 80% d-phenylalanine) and 0.33 g PPO. 3.5 mg CuCl and 6.7 mg DMAP were added as the catalyst.

10

TABLE 3:

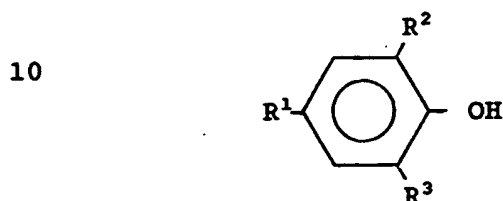
Example	Arms on dendrimer	% L-tyrosine	n	% PPO-arms in product
VI	8	100	22.5	8
VII	32	100	22.5	32
VIII	64	100	22.5	64
IX	64	80	22.5	51.2
X	64	50	22.5	32
XI	64	20	22.5	12.8

15

20

C L A I M S

1. Multihydroxy-functional oligophenylene oxide  
5 obtainable by reacting a compound containing hydroxyaryl comprising at least three hydroxyaryl groups according to the formula



- 15 where  
R<sup>1</sup> = an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,  
R<sup>2</sup>, R<sup>3</sup> = H or an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,  
20 or two of the R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> groups together constitute a ring structure containing 4-50 carbon atoms with a polyphenylene oxide in the presence of a catalyst complex comprising a transition metal and an amine.
- 25 2. Multi-hydroxy functional oligophenylene oxide according to claim 1, characterised in that the compound containing hydroxyaryl is a star-shaped phenol.
- 30 3. Multihydroxy-functional oligophenylene oxide according to claim 1, characterized in that the compound containing hydroxyaryl is a dendrimer containing terminal hydroxyaryl groups as defined in claim 1.
- 35 4. Mixture of a polyphenylene oxide and a multihydroxy-functional oligophenylene oxide according to any one of claims 1-3.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 95/00242

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08G65/48 C07C43/23 C07C41/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,1 119 914 (GENERAL ELECTRIC) 17 July 1968 see page 2, line 4 - page 5, line 45 ---	1-4
A	AM. CHEM. SOC. DIV. POLYMERS CHEM. PREPRINTS, vol.7, no.1, 1966 pages 166 - 172 G. D. COOPER ET AL 'The redistribution of hydroxyarylene ethers' see page 168 - page 169 ---	1-4
A	NL,A,6 803 930 (GENERAL ELECTRIC) 23 September 1968 see examples XXIX,XXX --- -/--	1-4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

29 September 1995

Date of mailing of the international search report

- 6. 10. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. ( + 31-70 ) 340-2040, T.x. 31 651 epo nl,  
Fax ( + 31-70 ) 340-3016

Authorized officer

Wright, M

# INTERNATIONAL SEARCH REPORT

Inter nal Application No  
PCT/NL 95/00242

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF ORGANIC CHEMISTRY., vol.34, no.2, February 1969, EASTON US pages 297 - 303 D. M. WHITE 'The synthesis of 4-hydroxyarylene ethers by the equilibration of phenols with poly(2,6-dimethyl-1,4-phenylene ether)' see page 297; document cited in the application ---	1-4
A	EP,A,0 550 209 (GENERAL ELECTRIC) 7 July 1993 see the claims; document cited in the application ---	1-4
A	EP,A,0 215 257 (BAYER) 25 March 1987 see the claims; document cited in the application -----	1-4



# INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/NL 95/00242

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
-GB-A-1119914		DE-A- 1720830	22-07-71
		FR-A- 1521881	26-07-68
		US-A- 3496236	17-02-70
		US-A- 3367978	06-02-68
-----			
NL-A-6803930	23-09-68	DE-A- 1770001	16-09-71
		FR-A- 1566600	09-05-69
		GB-A- 1202096	12-08-70
		US-A- 3392147	09-07-68
-----			
EP-A-0550209	07-07-93	CA-A- 2082695	01-07-93
-----			
EP-A-0215257	25-03-87	DE-A- 3529093	19-02-87
		JP-A- 62039628	20-02-87
-----			